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(19)

(54) A COMPOSITION FOR BONDING VULCANISED ARTICLES OF SATURATED OR UNSATURATED POLYOLEFIN RUBBER

(71) We, CHEMISCHE WERKE HÜLS AKTIENGESELLSCHAFT, a German Company, of 4370 Marl, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

This invention relates to compositions for bonding vulcanised articles of saturated or unsaturated polyolefin rubbers.

It is known that articles of vulcanised saturated or unsaturated polyolefin rubbers are used especially where high standards are set as regards resistance to weathering and ageing influences. Thus, for example, in the building trade, sheeting and film of ethylene-propylene copolymers or ethylene-propylene diene terpolymers are preferred as roof coverings. In this type of roofing the watertightness is determined to a great extent by the degree of success in water resistance in the joining or overlapping of the film or sheeting, a region which can give rise to great problems. The problem is usually solved by the use of strips of adhesive tape which often have to be activated prior to application by applying solvent or by thermal treatment (heating or exposure to a flame) in order to achieve firm adhesive contact with the film or sheeting.

It is therefore desirable to have adhesive tapes which already have such a high inherent tackiness that they can be used without any activation.

Adhesive tapes and compositions of this type based on isobutylene polymers (Information Brochure Oppanol B of BASF, pages 40 and 41, Oppanol is a Registered Trade Mark), or isobutylene-isoprene copolymers are known. There is need however for improvement in these self-adhesive compositions especially as regards their adhesion data at high temperatures and after ageing.

This invention seeks to provide improved compositions.

According to the invention there are provided compositions for bonding vulcanised articles of saturated or unsaturated polyolefin rubber, comprising

(a) 100 parts by weight of a polymer blend of from 20 to 70% by weight of an unvulcanised saturated or unsaturated polyolefin rubber and from 80 to 30% by weight of a polyisobutylene of a mean molecular weight (Mv) of less than 500,000;

(b) from 10 to 40, preferably from 20 to 40, parts by weight of an alkylphenol novolak with at least eight carbon atoms in the alkyl group; and

(c) from 20 to 50 parts by weight of one or more fillers.

Optionally the compositions also contain (d) auxiliaries for processing or preparing for processing and antiagers of the type and in the amounts customary in the rubber industry.

Vulcanised articles of saturated or unsaturated polyolefin rubber within the scope of this invention include articles and particularly film and sheeting based on ethylene-propylene copolymers, ethylene-propylene-diene or ethylene-butene-(1)-diene terpolymers, ethylene-propylene-butene-(1)-diene quaterpolymers and isobutylene-isoprene copolymers.

Particularly suitable saturated or unsaturated polyolefin rubbers for the production of compositions according to the invention include ethylene-propylene copolymers and ethylene-propylene-diene terpolymers and preferred diene components are dicyclopentadiene, hexadiene-1,4,5-methylene-2-norbornene, 5-ethylidene-2-norbornene and 5-isopropylidene-2-norbornene. These polymers may be prepared according to known prior art methods (German Laid-Open Specifications (DOS) Nos. 1,595,442, 1,720,450 and 1,570,352).

Polyisobutylene to be used according to the

invention may be prepared for example according to the method of French Patent Specification No. 1,508,766. It is essential that it should have a mean molecular weight ($\overline{M}v$, i.e. measured according to the viscosity methods) of less than 500,000 and preferably of from 100,000 to 350,000.

The alkylphenol novolaks of at least eight carbon atoms in the alkyl group to be used as component (b) may be prepared for example according to the method described in German Laid-Open Specification No. 1,569,482. Products of from nine to fifteen carbon atoms in the alkyl group are preferred.

Furnace carbon black and activated silicic acids such as are customarily used in processing rubber may be used as fillers for the adhesive compositions according to the invention.

The compositions according to the invention may contain optionally further components of the type and in the amount customarily added in the rubber industry (component (d)) as for example agents for processing or preparing for processing and antiagers. Examples of suitable processing auxiliaries are stearic acid, metal oxides, for example zinc oxide and lead oxide and to a certain extent also chloroparaffins which may also be regarded as auxiliaries for preparing for processing. Metal oxides and other conventional antiagers as for example mercaptobenzimidazole may serve as antiagers.

The compositions according to the invention may be used as pressure-sensitive tapes or may be sprayed as adhesive paste after a solvent has been added. The adhesive paste may be prepared by making 100 parts by weight of the composition according to the invention into a paste with from 50 to 150 parts by weight of a suitable solvent. Suitable solvents include hydrocarbons and chlorohydrocarbons as for example low boiling point gasolines, benzene, toluene, methylene chloride and trichloroethylene and mixtures of the same. It is preferred to use as component (a) for pressure sensitive tapes a polymer blend having from 60 to 80% by weight of polyisobutylene whereas for the adhesive paste a polyisobutylene fraction of from 30 to 60% by weight is suitable.

Adhesive pastes may be used not only for bonding overlapped film or sheeting but also for bonding the film or sheeting itself to a substrate such as concrete, plaster, flooring plaster or expanded plastics to assist or replace surface bonding by bituminous compositions or the like. The adhesion data are of the same order of magnitude as in overlapping bonding and in the same way are resistant to heat so that steep roofs or even vertical walls may be covered with film or sheeting in this way.

The properties of the compositions according to the invention, which represent a technical advance, are demonstrated by the following experimental Examples and Comparative Examples.

In all the Examples and Comparative Examples a roofing sheeting having a thickness of about 1mm based on an ethylene-propylene-5-ethylidene-2-norbornene terpolymer (eight double bonds per 1000 carbon atoms; Mooney viscosity ML—4, measured at 100° C., 100) is used which contains 130 parts of carbon black and 70 parts of plasticiser oil per 100 parts by weight of rubber and which has been cross-linked with sulphur. To test the adhesion of the bond in each case two strips of sheeting having the dimensions 2 cm×10 cm are doubled with inserted pressure-sensitive strips having a thickness of 1 mm. The strips of sheeting have previously been cleaned with a cloth moistened with gasoline as a safeguard. All the strips are cold and dry during doubling. The doubled specimens are loaded over the entire surface for five seconds with a weight of 30 kp and then immediately tested for separating strength according to DIN 53,274 (peeling test).

The tests are carried out at room temperature (RT=22° C.) and 75° C. and after an ageing period of one day and seven days are repeated in hot air at 100° C. in a Geer kiln.

When using a conventional commercial pressure-sensitive tape based on an isobutylene polymer the following values are obtained in this way (Comparative experiment):

Adhesion data in kp per cm of strip width:	*RT*	*75° C.*
initial adhesion	0.5	0.05
after ageing at 100° C. for one day in a Geer kiln	0.9	0.10
after ageing for seven days at 100° C. in a Geer kiln	0.9	0.03

Clearly improved values after ageing are achieved with the following experimental formulations (Examples 5 to 7, as compared with Comparative Examples 1 to 4 and 8):

Components:

(A) unvulcanised ethylene-propylene-5-ethylidene-2-norbornene rubber (eight double bonds per 1000 carbon atoms, ML at 100° C. 70); Examples 1 to 8, 50 parts each;

(B) polyisobutylene ($\overline{M}v$ 400,000); 50 parts each, Ex. 1 to 8;

(C) zinc oxide, red seal; 3 parts each Examples 1 to 8;

(D) stearic acid; 0.60 part each, Examples 1 to 8;

(E) FEF carbon black; 12.50 parts each, Examples 1 to 8;

(F) activated silicic acid; 12.50 parts each, Examples 1 to 8;

(G) chloroparaffin 70%; Example 1, 15 parts;

(H) alkyd resin; Example 2, 15 parts;

(I) highly chlorinated diphenyl; Example 3, 15 parts;

(J) phenol-acetylene condensation resin; Example 4, 15 parts;

(K) alkylphenol novolak (the alkylphenol containing 9 carbon atoms in the alkyl chain); Example 5, 10 parts; Example 6, 20 parts; Example 7, 40 parts; Example 8, 80 parts.

Adhesion values in kp/cm of strip width:

In the following Table:

(L)=initial adhesion at RT/75° C.
(M)=adhesion after 1 day ageing at 100° C. in a Geer Kiln
(N)=adhesion after 7 days ageing at 100° C. in a Geer Kiln at RT/75° C.

Example	(L)	(M)	(N)
1	0.25/0.05	0.9/0.30	1.50/0.40
2	0.20/0.05	0.9/0.20	1.50/0.30
3	0.20/0.05	0.75/0.20	1.10/0.20
4	0.35/0.05	0.9/0.20	1.50/0.30
5	0.35/0.05	1.0/0.30	2.20/0.50
6	0.50/0.05	1.20/0.40	4.50/1.00
7	0.50/0.05	1.20/0.40	4.00/0.90
8	0.50/0.05	1.10/0.30	2.00/0.60

In this series an improvement in the ageing adhesion values is evident by the blending of polyisobutylene with EPDM and the superiority of alkylphenol novolak over other tackifiers. Examples 1 to 4 and 8 are included solely for comparison.

In the following Examples 9 to 13 a polyisobutylene having a mean molecular weight $\bar{M}v$ of about 200,000 is used instead of the medium viscosity polyisobutylene having an $\bar{M}v$ of 400,000. Example 9 is included solely for comparison

Example	9	10	11	12	13
unvulcanised ethylene-propylene-5-ethylidene-2-norbornene rubber (8db/1000 C, NL–4 at 100°C:70)	–	50	35	25	20
polyisobutylene (Mv = 200,000)	100	50	65	75	80
zinc oxide, red seal	3	3	3	3	3
stearic acid	0.50	0.50	0.50	0.50	0.50
antiager DDA	–	0.30	0.30	0.30	0.30
FEF carbon black	8	10	10	10	10
activated silicic acid	8	10	10	10	10
chloroparaffin 70%	–	15	15	15	15
alkylphenol novolak*	15	15	15	15	15

* the alkyl phenol having 9 carbon atoms in the alkyl chain.

Adhesion values in kp per cm of strip width:

Example	(L)	(M)	(N)
9	0.70/0.30	1.00/0.10	0.80/0.04
10	0.20/0.50	1.40/0.40	4.50/0.90
11	0.40/0.08	1.30/0.30	4.40/0.85
12	0.90/0.07	1.00/0.25	3.60/0.80
13	0.70/0.05	0.90/0.20	2.50/0.30

The chloroparaffin used in the Examples serves as an auxiliary for processing and preparation for processing and brings better adhesion values than other auxiliaries as for example hydrocarbon resins.

The following is a recipe for the production of a sprayable adhesive paste (Example 14):

unvulcanised ethylene-propylene-5-ethylidene-2-norbornene rubber (eight double bonds per 1000 carbon atoms, ML—4 at 100° C: 70)	55
polyisobutylene ($\overline{M}v$=200,000)	45
zinc oxide, red seal	3
stearic acid	0.30
FEF carbon black	10
activated silicic acid	12
chloroparaffin	10
alkylphenol novolak (having 9 carbon atoms in the alkyl chain of the alkyl phenol)	15
solvent mixture	150

The solvent mixture consists of 80% of a low boiling point gasoline and 20% of toluene. The adhesive paste is prepared in a solution kneader and applied to the sheeting in a layer having a thickness of about 1.2 mm by means of the cartridge spraying method. After exposure to the air for fifteen to twenty minutes the sheeting is prepared with the hand roller and tested as above.

Adhesion values in kp per cm of strip width:

Example	(L)	(M)	(N)
14	0.70/0.10	1.30/0.30	3.30/1.20

WHAT WE CLAIM IS:—

1. A composition for bonding vulcanised articles of saturated or unsaturated polyolefin rubber, comprising

(a) 100 parts by weight of a polymer blend of from 20 to 70% by weight of an unvulcanised saturated or unsaturated polyolefin rubber and from 80 to 30% by weight of a polyisobutylene of a mean molecular weight ($\overline{M}v$) of less than 500,000;
(b) from 10 to 40 parts by weight of an alkylphenol novolak with at least eight carbon atoms in the alkyl group; and
(c) from 20 to 50 parts by weight of one or more fillers.

2. A composition according to claim 1, wherein an ethylene-propylene rubber is used as the polyolefin rubber.

3. A composition according to claim 1, wherein an ethylene-propylene-diene rubber is used as the polyolefin rubber.

4. A composition according to claim 3, wherein the ethylene-propylene-diene rubber contains dicyclopentadiene, hexadiene-1,4,5-methylene-2-norbornene, 5-ethylidene-2-norbornene or 5-isopropylidene-2-norbornene as the diene.

5. A composition according to any of claims 1 to 4, wherein a polyisobutylene is used which has a mean molecular weight ($\overline{M}v$) of from 100,000 to 350,000.

6. A composition according to any of claims 1 to 5, wherein an alkylphenol novolak is used which has from nine to fifteen carbon atoms in the alkyl group.

7. A composition according to any of claims 1 to 6, wherein carbon black and/or activated silicic acid is used as filler.

8. A composition according to any of claims 1 to 7, containing from 20 to 40 parts by weight of the alkylphenol novolak (b) per 100 parts by weight of the polymer blend (a).

9. A composition according to claim 1 and

substantially as described in any of the foregoing Examples 5 to 7 and 10 to 14.

10. Vulcanised articles of saturated or unsaturated polyolefin rubber when bonded with the aid of a composition according to any of claims 1 to 9.

11. Self-adhesive tape produced with the use of a composition according to any of claims I to 9.

12. A process for the production of a sprayable adhesive paste which comprises adding from 50 to 150 parts by weight, based on 100 parts by weight of adhesive composition, of a solvent to a composition according to any of claims 1 to 9.

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